

Hydrogen-bonded Silica Gels Dispersed in a Smectic Liquid Crystal: A Random Field XY System

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The effect on the nematic to smectic-A transition in octylcyanobiphenyl (8CB) due to dispersions of hydrogen-bonded silica (aerosil) particles is characterized with high-resolution x-ray scattering. The particles form weak gels in 8CB creating a quenched disorder that replaces the transition with the growth of short range smectic correlations. The correlations include thermal critical fluctuations that dominate at high temperatures and a second contribution that quantitatively matches the static fluctuations of a random field system and becomes important at low temperatures.

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Quenched disorder in condensed matter systems can profoundly affect their thermodynamic behavior, creating unique challenges for statistical mechanics. For fluids, confinement within a random porous medium offers a convenient method for introducing such disorder, and studies of superfluid helium¹ and binary liquids² in aerogels – rigid, highly-porous chemically-bonded silica gels – have led to insights into the implications of disorder on phase transitions. Similarly, the fragile nature of the mesomorphic phases of liquid crystals and their sensitivity to surface interactions make these systems well suited for studies within porous media. In particular, the nematic (N) to smectic-A (SmA) transition, which typically exhibits anisotropic 3D-XY critical behavior, offers an ideal case for understanding the effects of a random environment on continuous symmetry fluctuations. The demonstration through x-ray scattering^{3,4} and calorimetry⁵ of the destruction of the N-SmA transition by confinement in aerogels has shed light on these effects. Detailed theoretical work has further elucidated the fragility of the smectic phase to arbitrarily weak quenched disorder and has introduced the possibility that for sufficiently weak disorder novel “Bragg glass” phases may become stable⁶.

In an effort to probe liquid crystals with increasingly weak disorder in a controlled way, we have conducted a high-resolution x-ray scattering study of the effect of hydrogen-bonded silica (aerosil) gels on the N-SmA transition in octylcyanobiphenyl (8CB). We find that the constraints imposed by these weakly-connected gels profoundly alter the smectic ordering, leading to behavior quantitatively like that induced by random fields. Random field systems have been fruitful models for exploring theoretically effects of quenched disorder, and random field Ising magnets have provided the primary experimental testing ground for these ideas⁷. 8CB in porous silica thus introduces an opportunity to make experimental contact with random field theories for a transi-

tion that breaks a continuous symmetry^{6,8–10}. Consistent with theoretical predictions, we find that the smectic phase is destroyed by the disorder and is replaced by the growth of short-range smectic correlations. The low-temperature correlation length exceeds the typical void size in the gels by approximately a factor of four, consistent with the picture of the aerosil creating a weak to intermediate disorder. The temperature dependence of the correlation function for different densities of gel further indicates that the disorder suppresses nematic fluctuations in the liquid crystal.

The smectic state is distinguished from the nematic by a one-dimensional modulation in density, and a two-component order parameter specifying the amplitude and phase of the modulation characterizes the N-SmA transition. To introduce quenched disorder, we disperse in the 8CB hydrophilic aerosil, 70 Å diameter silica particles coated with hydroxyl groups. At volume fractions above roughly 1%, these particles form a hydrogen-bonded thixotropic gel, and interactions between the surfaces of the gel and liquid crystal molecules (“anchoring”) introduce locally preferred orientations and phases to the smectic ordering that compete with the globally uniform order of the pure smectic. Aerosil gels have strong similarities with aerogels but represent a weaker disorder for the smectic in two essential respects. First, the ability to grow the aerosil gel directly within the liquid crystal permits structures of higher porosity. Also, as discussed below, for a given silica density the hydrogen-bonded aerosils perturb the smectic ordering less severely than rigid aerogels. However, consistent with recent studies^{11,12} we find that aerosils above 1% volume fraction create a reproducible, density-dependent quenched disorder. In our experiments we have tuned the strength of this disorder by varying the density of silica, ρ_s , from 0.025 grams of SiO₂ per cm³ of 8CB, just above the gelation threshold, to 0.341 grams of SiO₂ per cm³ of 8CB.

Reference¹¹ provides details of the sample preparation and fractal structure of aerosil gels.

To characterize the effect of the aerosil gels on the N-SmA transition, we have measured with x-ray scattering the static structure factor, $S(q)$, which provides direct information about the correlation function of the smectic order. The experiments were conducted on the X20 beamline of the National Synchrotron Light Source using 8 keV photons. 1 mm thick samples were held between kapton sheets in an oven containing dry nitrogen gas, and the scattering was performed in transmission geometry. Following prolonged exposure to the x-rays, the 8CB with dispersed aerosil displayed evidence of damage, including progressively degraded smectic order. Therefore, we carefully limited the exposures to levels below which any damage was detectable.

Figure 1 shows representative x-ray scattering line-shapes for two values of ρ_s . In accord with theoretical predictions of Radzihovsky, Toner, *et al.*^{6,13}, for all densities and for the full experimental temperature range, the diffraction peak corresponding to smectic layering is markedly broader than the resolution-limited peak measured for pure 8CB in the SmA phase, demonstrating the destruction of the smectic long range order by the aerosil. We model this short-ranged order with a structure factor containing two contributions:

$$S(q) = \frac{\sigma_1}{1 + (q_{\parallel} - q_0)^2 \xi_{\parallel}^2 + q_{\perp}^2 \xi_{\perp}^2 + c q_{\perp}^4 \xi_{\perp}^4} + \frac{\sigma_2 (\xi_{\parallel} \xi_{\perp}^2)}{(1 + (q_{\parallel} - q_0)^2 \xi_{\parallel}^2 + q_{\perp}^2 \xi_{\perp}^2 + c q_{\perp}^4 \xi_{\perp}^4)^2} \quad (1)$$

where the wave vector q_{\parallel} is along the smectic layer normal and q_{\perp} is perpendicular to it.

The first term in $S(q)$, an anisotropic Lorentzian with quartic corrections, is the form for the susceptibility in pure nematic 8CB and describes the critical thermal fluctuations on approaching the N-SmA transition¹⁴. The second term, which is simply proportional to this susceptibility squared, is designed to account for static fluctuations induced by the quenched disorder. This term is motivated by studies on random field Ising magnets in which such an expression has been shown to describe accurately the short-range correlations induced by the static fluctuations¹⁵ and has been justified theoretically^{16,17}. In the limit of long range order, the second term evolves into a Bragg-peak, $\sigma_2 \delta(q_{\parallel} - q_0) \delta(q_{\perp})$ ¹⁸. The solid lines in Fig. 1 are the results of fits to the powder average of Eq. (1) convolved with the experimental resolution function. The measured scattering profile also includes a temperature-independent, sloping background from the aerosil gel, shown in the figures as dashed lines. As Fig. 1 illustrates, Eq. (1) provides an excellent description of the lineshape over a wide range of temperatures and aerosil densities. In these fits, we have taken ξ_{\perp} and c as functions of ξ_{\parallel} , with $\xi_{\perp}(\xi_{\parallel})$ and $c(\xi_{\parallel})$ set by their relations in pure 8CB, which are known to high precision¹⁴. Thus, each fit has only four free parameters – q_0 , ξ_{\parallel} , σ_1 , and

σ_2 – with two parameters, ξ_{\parallel} and σ_2/σ_1 , controlling the shape of the peaks.

At temperatures near and above the N-SmA transition temperature for pure 8CB, $T_{NA}^0 = 306.98K$ ¹¹, the measured lineshapes in the aerosil samples are described very well by the thermal fluctuation term alone (i.e., $\sigma_2 = 0$). Thus, for $T > T_{NA}^0$, the smectic correlations in aerosil samples are very similar to the critical fluctuations of the pure liquid crystal. Figure 2(a) displays ξ_{\parallel} for a series of aerosil densities in this high temperature region. The solid line in the figure, ξ_{\parallel} for pure 8CB (aligned in the nematic by a magnetic field)¹⁴, demonstrates the strong similarity between thermal fluctuations in the pure liquid crystal and in the liquid crystal with dispersed aerosil. At these high temperatures, ξ_{\parallel} is smaller than the average void size, l_o , in the gels, and the influence of the gel is minimal. (The values of l_o range from 200 Å for $\rho_s = 0.341$ to 2650 Å for $\rho_s = 0.025$ ¹¹.) Rather than follow the diverging behavior associated with a thermodynamic transition, however, ξ_{\parallel} for 8CB with dispersed aerosil deviates from that of pure 8CB as the temperature decreases, and the smectic correlations remain short-ranged. Figure 2(b) shows the behavior of ξ_{\parallel} for four values of ρ_s to low temperatures. The susceptibility, σ_1 , for 8CB with dispersed aerosil similarly tracks that of the pure system at high temperatures but fails to diverge.

We stress the importance of including the quartic term ($c > 0$) in Eq. (1) to account correctly for the temperature dependence of the lineshapes. The values of c vary from approximately 0.25 for $\xi_{\parallel} = 50\text{Å}$, its value 4 K above T_{NA}^0 , to less than 0.02 for $\xi_{\parallel} > 10^4\text{Å}$ ¹⁴. At high temperatures, when $c \approx 0.25$, the thermal fluctuation term is effectively the square of a Lorentzian along q_{\perp} , leading to a powder-averaged lineshape that strongly resembles a Lorentzian. As ξ_{\perp} increases on cooling and c decreases, the powder average of the first term in Eq. (1) deviates strongly from a Lorentzian, and the tails of the lineshape become more pronounced. We note that the x-ray lineshapes of 8CB in rigid aerogels resemble this behavior⁴. The analysis by Rappaport *et al.* of the aerogel results, however, differs significantly from that presented here. In particular, no measurable signal from thermal fluctuations was reported for 8CB in aerogel^{3,4}.

At temperatures below T_{NA}^0 , deviations from the form describing the critical behavior of pure 8CB become apparent in the lineshape of 8CB with dispersed aerosil, particularly for large ρ_s . These deviations indicate an increasing importance of interactions with the gel, rather than intrinsic thermal fluctuations, in determining the smectic correlations. The second term in Eq. (1) describing random-field induced, short-range order accounts for these changes in the correlations very well. Figure 3 displays σ_2 as a function of temperature for two representative values of ρ_s . The rapid growth of σ_2 on cooling reflects the dominance of these random-field static fluctuations at low temperatures. In this low temperature region, ξ_{\parallel} reaches an essentially temperature-independent

value, as Fig. 2(b) illustrates. Figure 4 displays the low temperature correlation lengths, ξ_{\parallel}^{LT} as a function of ρ_s . The solid line in Fig. 4 is the result of a fit to the nematic correlation lengths of the homolog 6CB with dispersed aerosils measured by Bellini *et al.*¹⁹ with static light scattering. These light scattering studies demonstrate that the nematic order in a liquid crystal with dispersed aerosil breaks up into very large, but finite, domains. Since the smectic layering forms within these nematic domains, the nematic domain sizes naturally set upper limits for the range of the smectic correlations. However, ξ_{\parallel}^{LT} remains well below these limits for all ρ_s , demonstrating the sensitivity of the smectic phase to quenched disorder. The dashed line in Fig. 4 is the mean aerosil void size, l_0 , as a function of ρ_s ¹¹. For the range of densities studied, the ratio of ξ_{\parallel}^{LT} to l_0 is nearly independent of density and is roughly equal to four, consistent with an intermediate strength disordering field. This result contrasts with the smectic ordering in aerogel³ for which the measured correlation lengths barely exceed the void sizes, illustrating again the weaker nature of disorder induced by aerosil.

At low temperatures (where c approaches a constant value) σ_2 is proportional to the integrated intensity of the static fluctuation term in $S(q)$. The growth of this intensity strongly resembles that of an order parameter squared, and the solid lines in Fig. 3 are the results of fits to the form $\sigma_2 \propto (T_2 - T)^x$, where both x and T_2 depend on ρ_s . The inset of Fig. 3 displays the change in x with ρ_s . We emphasize that x is an effective exponent since the aerosil destroys the true N-SmA phase transition. However, associating the integrated intensity from the static, short-range correlations with an order parameter squared (so that $x = 2\beta$), we observe that the effective exponent spans the range from near the tricritical value (like with pure 8CB) at small ρ_s to 3D XY-like at large ρ_s . For pure liquid crystals, the measured critical behavior at the N-SmA transition is affected by couplings between the nematic and smectic order parameters (de Gennes coupling)²⁰. The variation of x with ρ_s suggests that the quenched disorder suppresses the nematic susceptibility that drives the critical behavior of the pure system away from 3D-XY universality. This result agrees nicely with specific heat studies of 8CB with dispersed aerosil which show the effective heat capacity exponent, α , decreasing toward the 3D-XY value with increasing ρ_s ^{11,21}.

In conclusion, these x-ray scattering studies have shown that 8CB with dispersed aerosil provides a model random field system for a transition that breaks a continuous symmetry. In particular, the success of Eq. (1) in describing the smectic correlations and the corresponding behaviors of ξ_{\parallel} and σ_2 form a compelling picture in which the aerosil gel creates a random local-orienting field that destroys the N-SmA transition, consistent with theoretical predictions⁶. In the random field Ising magnet, slow dynamics and non-equilibrium effects strongly influence the behavior^{22,23}. Efforts to observe hysteretic or time

dependent behavior indicative of metastability in these scattering measurements or in the calorimetry studies¹¹ on 8CB with dispersed aerosil revealed no such effects. These results suggest that the continuous symmetry allows the system to find equilibrium efficiently, even in the presence of random fields, in marked contrast to the behavior in random field Ising systems⁷. However, a better understanding of the dynamics would be beneficial for placing the observed ordering in the context of equilibrium statistical mechanics.

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FIG. 1. X-ray scattering intensity for 8CB with dispersed aerosil for $\rho_s = 0.025$ g/cm³ at (a) 288.5 K and (b) 307.6 K and $\rho_s = 0.282$ g/cm³ at (c) 300.6 K and (d) 306.6 K. The solid lines are the results of fits to the powder average of Eq. (1) convolved with the experimental resolution and the dashed lines are the temperature independent background due to scattering from the aerosil gel. The higher temperature lineshapes, (b) and (d), are due to thermal critical fluctuations as in pure 8CB while the low temperature lineshapes, (a) and (c), have forms expected for short-range correlations dominated by static, random-field induced fluctuations.

FIG. 2. The parallel correlation length, ξ_{\parallel} , as a function of temperature (a) at high temperature for a series of aerosil densities: $\rho_s = 0.025$ (\circ), 0.041 (\bullet), 0.051 (filled diamond), 0.078 (open box), 0.105 (∇), 0.161 (\triangle), 0.220 (filled box), 0.282 (filled triangle), and 0.341 (filled upside-down triangle); and (b) on an expanded scale to low temperature for four values of ρ_s . The solid line is ξ_{\parallel} for pure 8CB [14].

FIG. 3. The integrated intensity of the static fluctuation term, σ_2 , as a function of temperature for $\rho_s = 0.025$ (\bullet) and $\rho_s = 0.220$ (\circ). The absolute magnitudes of σ_2 for each ρ_s are arbitrary and should not be compared. The solid lines are fits to $\sigma_2 \propto (T_2 - T)^x$. The inset shows x versus ρ_s . The effective exponent x spans the range for an order parameter exponent from near the tricritical value, 0.5, at small ρ_s to the 3D XY value, 0.69, at large ρ_s .

FIG. 4. Low temperature correlation lengths, ξ_{\parallel}^{LT} versus ρ_s . The solid line is the nematic correlation length (for 6CB) [19], and the dashed line is the mean aerosil void size, l_0 .

Figure 1 S. Park et al.

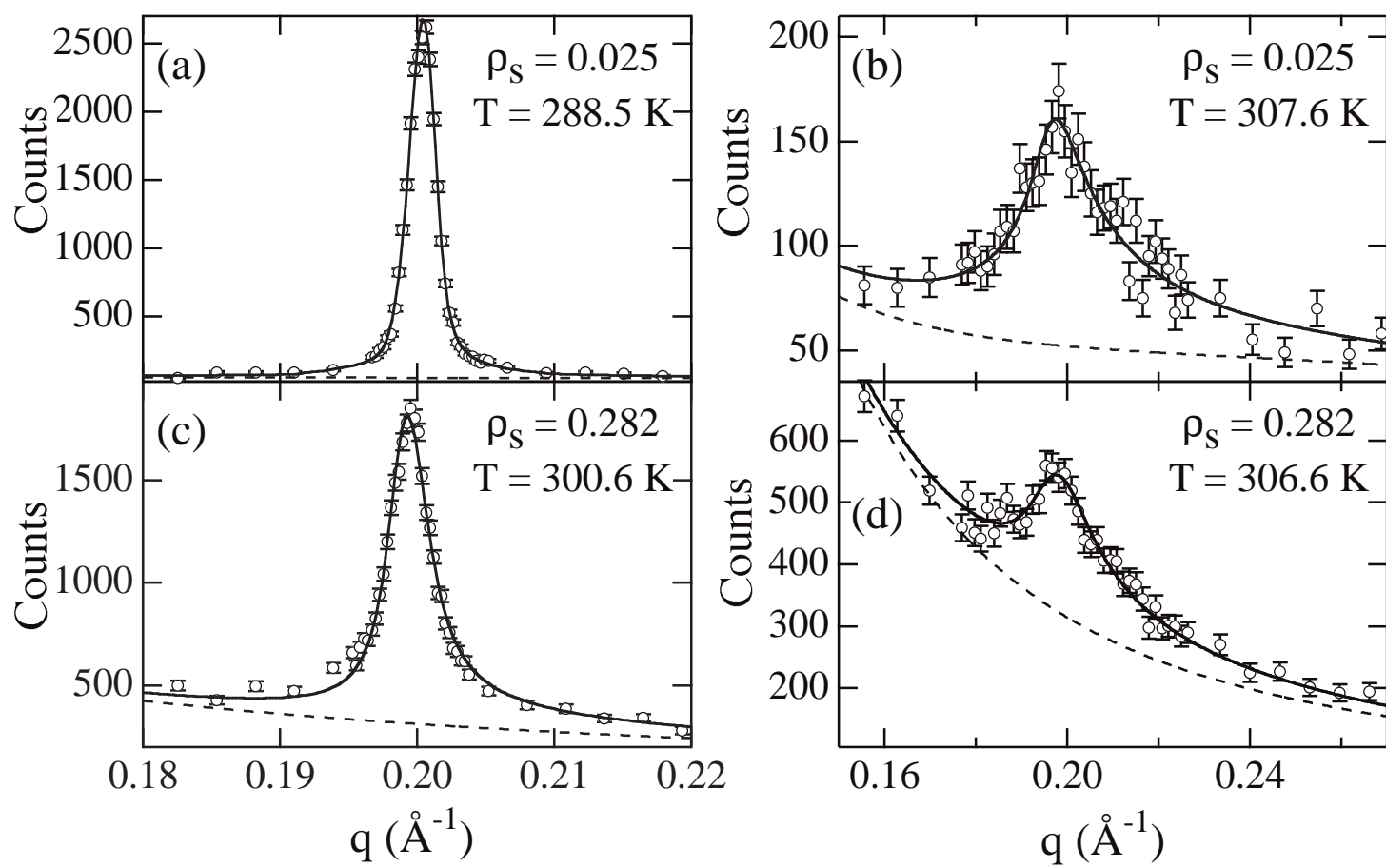


Figure 2 S. Park et al.

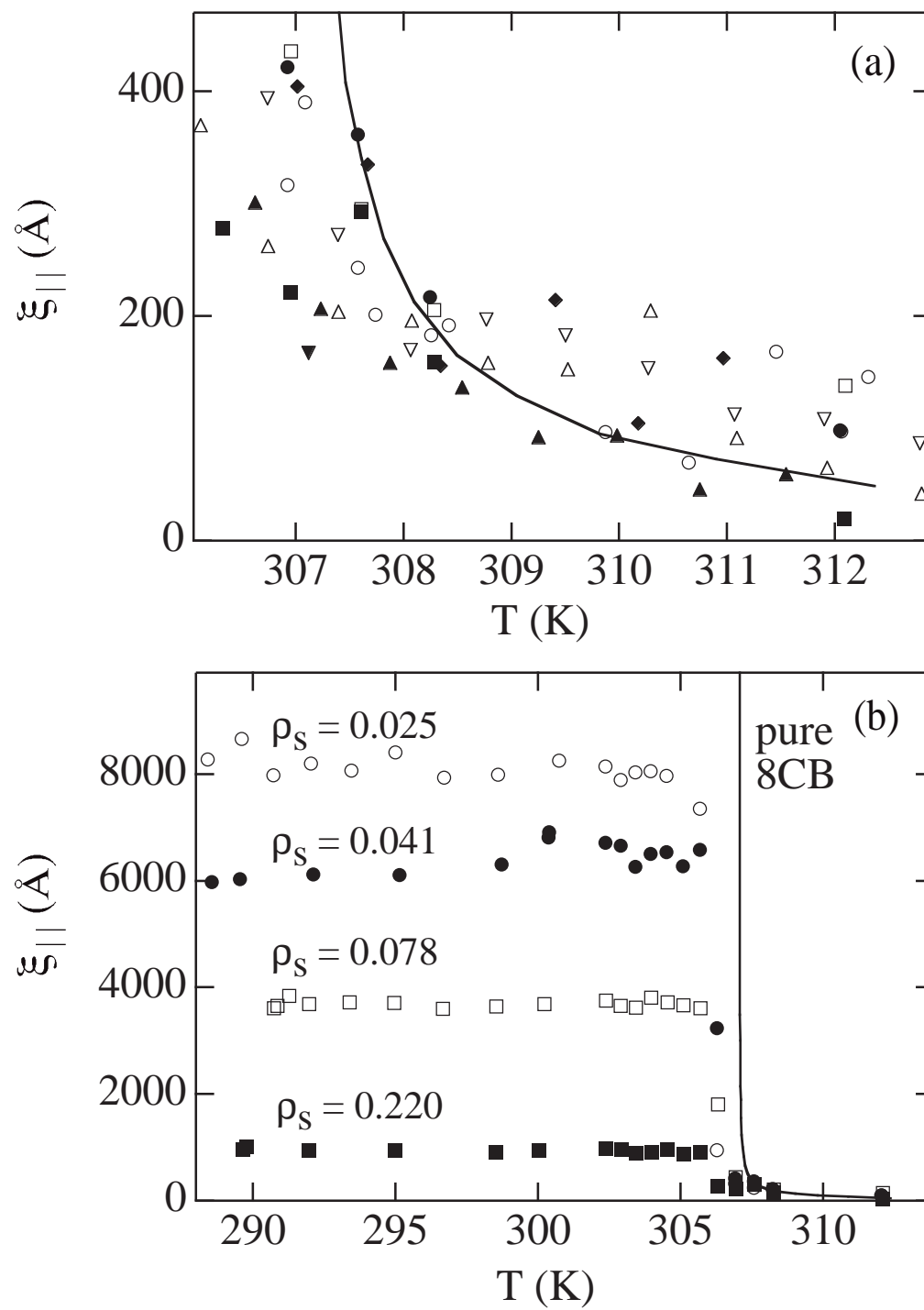


Figure 3 S. Park et al.

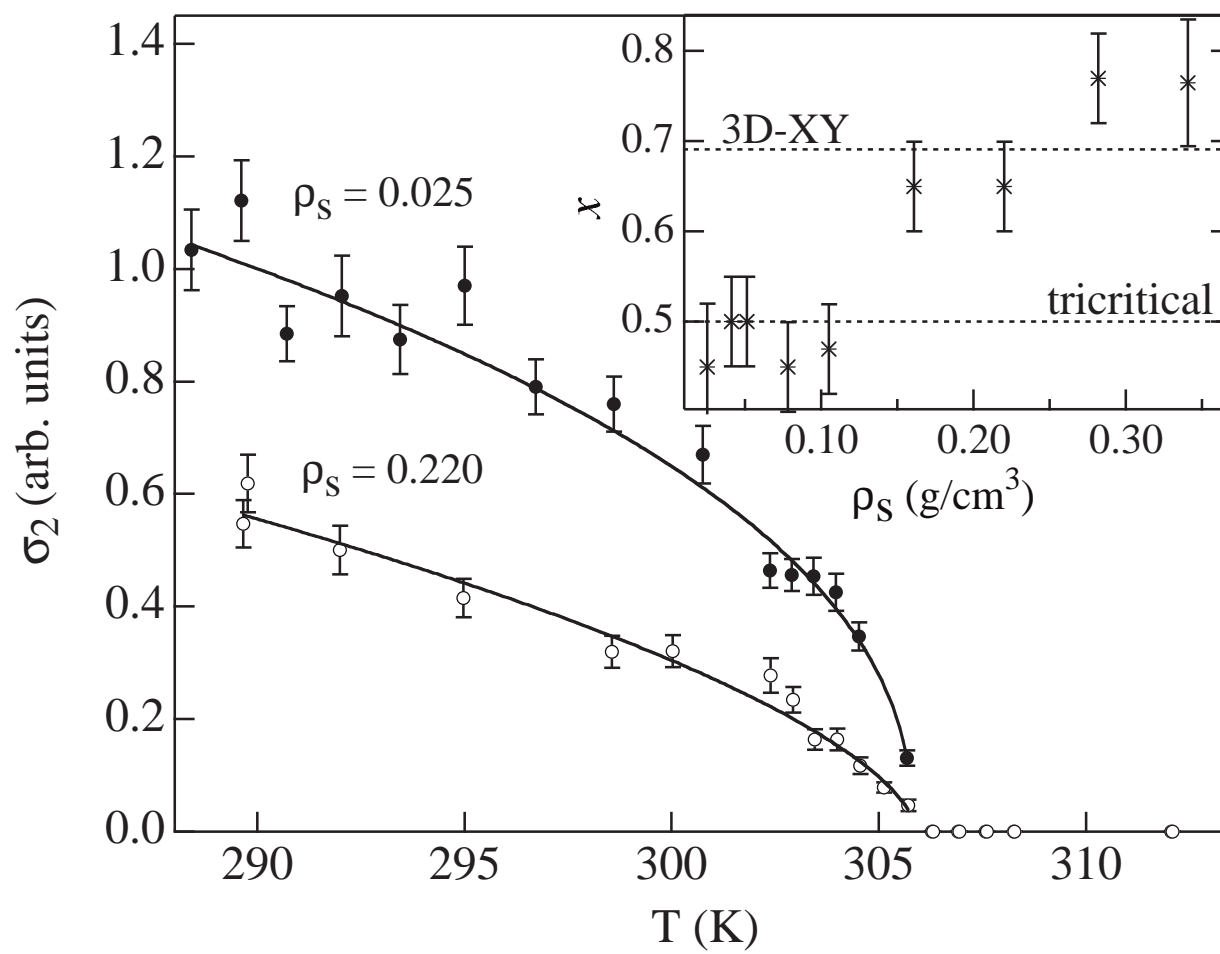


Figure 4 S. Park et al.

